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$Na_2CdGe_2Q_6$ (Q = S, Se): two metal-mixed chalcogenides with phase-matching abilities and large second-harmonic generation responses

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1. Tables and Figures

2. References

Table S1. Atomic bond-valence and isotropic displacement parameters for title compounds.

$Na_2CdGe_2S_6$

toms	S.O.F.	x	y	z	U(eq)	BVS
Na(1)	1	0.3778(5)	0.3000(3)	0.7196(3)	0.052(1)	0.970
Na(2)	1	-0.0219(5)	0.5115(2)	0.3514(3)	0.051(1)	0.964
Cd(1)	1	0.8114(1)	0.2513(1)	0.5591(1)	0.023(1)	2.185
Ge(1)	1	0.4371(1)	0.3628(1)	0.3366(1)	0.017(1)	4.076
Ge(2)	1	0.6212(1)	0.5247(1)	0.5852(1)	0.016(1)	4.080
S(1)	1	0.8823(2)	0.4453(1)	0.5758(2)	0.024(1)	1.967
S(2)	1	0.3655(2)	0.4341(1)	0.5027(1)	0.022(1)	1.993
S(3)	1	0.11285(2)	0.1869(1)	0.5295(2)	0.023(1)	1.893
S(4)	1	0.5909(3)	0.4994(1)	0.2742(1)	0.027(1)	2.247
S(5)	1	0.6068(2)	0.2206(1)	0.3640(1)	0.023(1)	2.156
S(6)	1	0.1764(2)	0.3436(1)	0.2200(1)	0.025(1)	2.018

$Na_2CdGe_2Se_6$

atoms	S.O.F.	x	y	z	U(eq)	BVS
Na(1)	1	0.6702(13)	0.2986(6)	0.3087(8)	0.057(2)	0.965
Na(2)	1	0.5656(11)	0.066(5)	0.6814(7)	0.048(2)	0.988
Cd(1)	1	0.2355(2)	0.2501(1)	0.4722(1)	0.028(1)	2.268
Ge(1)	1	0.4292(2)	0.5231(1)	0.4454(1)	0.019(1)	4.094
Ge(2)	1	0.6129(2)	0.3611(1)	0.6935(2)	0.019(1)	4.093
Se(1)	1	0.4557(3)	0.4977(1)	0.2527(2)	0.027(1)	2.225
Se(2)	1	0.3763(2)	0.1550(1)	0.3159(2)	0.030(1)	2.042
Se(3)	1	0.6923(2)	0.4323(1)	0.5264(1)	0.023(1)	2.020
Se(4)	1	0.1609(2)	0.4435(1)	0.4549(2)	0.025(1)	1.975
Se(5)	1	0.4412(2)	0.2158(1)	0.6646(1)	0.029(1)	2.208
Se(6)	1	-0.0844(3)	0.1882(1)	0.5014(2)	0.027(1)	1.917

Table S2. A series of IR materials with structural transformation.

$AgGaS_2$[1a]	-42*m*	tetragonal	$Li_2In_2SiSe_6$[20]	*Cc*	monoclinic
$AgGaSe_2$[1b]			$Li_2In_2GeS_6$[20]		
$AgGaTe_2$[1c]	*I*-42*d*		$Li_2In_2GeSe_6$[20]		
$LiGaTe_2$[2]			$Na_2Hg_3Ge_2S_8$[21]	$P\bar{4}c2$	tetragonal
$LiInTe_2$[2]			$Na_2Hg_3Si_2S_8$[21]		
$LiAlTe_2$[2]			$Na_2Hg_3Sn_2S_8$[21]		
$LiGaS_2$[2]	*Pna*21	orthorhombic	$K_2Hg_3Ge_2S_8$[22]	*Aba*2/*C*2	orthorhombic/monoclinic
$LiInS_2$[2]			$Rb_2Hg_3Ge_2S_8$[23]	*P*21/*c*	monoclinic
$LiGaSe_2$[2]			$Rb_2Hg_3Sn_2S_8$[23]		
$LiInSe_2$[2]			$Cs_2Hg_3Ge_2S_8$[23]	*P*-1	triclinic
$LiAlS_2$[2]			$Cs_2Hg_3Sn_2S_8$[23]		
$LiAlSe_2$[2]			$KCd_4Ga_5S_{12}$[24]	*R*3	trigonal
$NaAsSe_2$[3]	*Pca*21		$RbCd_4Ga_5S_{12}$[24]		
$Na_2Ge_2S_5$[4]	*Cmcm*	orthorhombic	$CsCd_4Ga_5S_{12}$[24]		
$Na_2Ge_2Se_5$[5]	*Pna*21		$CsMn_4In_5Te_{12}$[25]		
$KPSe_6$[6]	*Pca*21	orthorhombic	$CsZn_4In_5Te_{12}$[25]		
$RbPSe_6$[6]			$CsCd_4In_5Te_{12}$[25]		
$CsPSe_6$[6]	*P*2/*n*	monoclinic	$Cs_2ZnGe_3S_8$[26]	*P*21/*c*	monoclinic
$BaGa_4S_7$[7]	*Pmn*21	orthorhombic	$Cs_2ZnGe_3Se_8$[26]	$P2_12_12_1$	orthorhombic
$BaGa_4Se_7$[8]	*Pc*	monoclinic	$Cs_2ZnGe_3Te_8$[26]		
$BaAl_4Se_7$[9]			$Cs_2CdGe_3S_8$[26]		
$SnGa_4S_7$[10]			$Cs_2CdGe_3Se_8$[26]		
$SnGa_4Se_7$[10]			$Cs_2MgGe_3Se_8$[26]		
$PbGa_4S_7$[20]			Ba_3GaS_4Cl[27]	*Pnma*	orthorhombic
Cd_4SiS_6[11]	*Cc*	monoclinic	Ba_3GaS_4Br[27]		
Cd_4SiSe_6[12]			Ba_3GaSe_4Cl[27]		
Cd_4GeS_6[13]			Ba_3InSe_4Cl[27]	*I*4/*mcm*	teragonal
Cd_4GeSe_6[14]			Ba_2BiGaS_5[28]	*Pnma*	orthorhombic
Hg_4SiS_6[15]	*Cc*	monoclinic	Ba_2BiInS_5[28]	*Cmc*2$_1$	
Hg_4SiSe_6[15]			$Ba_4CuGa_5S_{12}$[29]	$P\bar{4}2_1c$	tetragonal
Hg_4GeS_6[16]			$Ba_4CuGa_5Se_{12}$[29]		
Li_2ZnSnS_4[17]	*Pn*	orthorhombic	$BaGa_2SiS_6$[30]	*R*3	trigonal
$Li_2ZnGeSe_4$[18]			$BaGa_2GeS_6$[30]		
$Li_2ZnSnSe_4$[18]			$BaGa_2SiSe_6$[30]		
Li_2CdGeS_4[19]	*Pmn*2$_1$		$BaGa_2GeSe_6$[30]		
Li_2CdSnS_4[19]			$PbGa_2SiSe_6$[31]	*Cc*	monoclinic
$Li_2In_2SiS_6$[20]	*Cc*	monoclinic	$PbGa_2GeSe_6$[31]	*Fdd*2	orthorhombic

Table S3. Dipole moment calculations for $Na_2CdGe_2S_6$ and $Na_2CdGe_2Se_6$.

$Na_2CdGe_2S_6$

species	dipole moment				
				magnitude	
	x (a)	*y (b)*	*z (c)*	debye	$\times 10^{-4}$ esu·cm /Å^3
$Cd(1)S_4$	6.80	0.00	-9.98	12.07	0.05
$Ge(1)S_4$	-4.63	0.00	3.09	5.56	0.02
$Ge(2)S_4$	1.64	0.00	16.68	16.76	0.06
Unit cell	3.81	0.00	9.79	10.51	0.04

$Na_2CdGe_2Se_6$

species	dipole moment				
				magnitude	
	x (a)	*y (b)*	*z (c)*	debye	$\times 10^{-4}$ esu·cm /Å^3
CdSe4	-8.74	0.00	13.84	16.37	0.05
Ge(1)Se4	-2.17	0.00	-25.47	27.02	0.09
Ge(2)Se4	6.66	0.00	-6.04	11.55	0.04
Unit cell	-4.25	0.00	-17.67	35.57	0.12

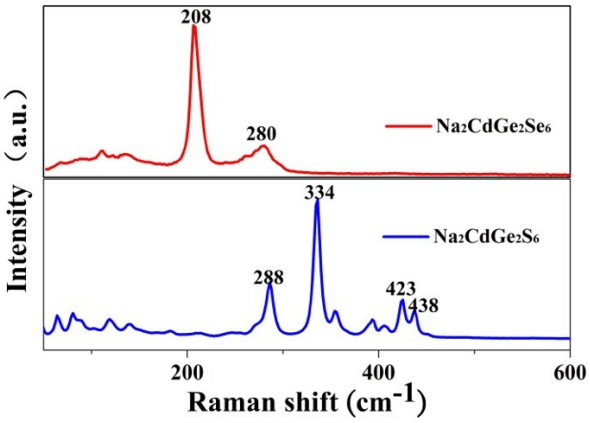

Fig. S1. Raman spectra for title compounds.

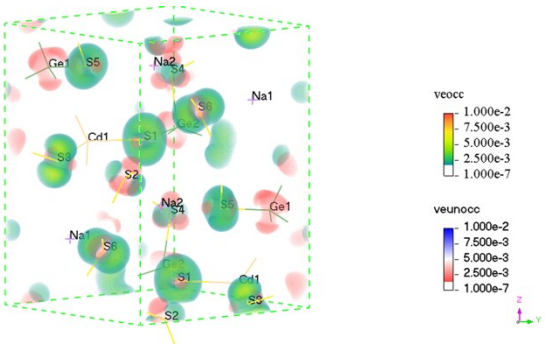

Fig. S2. SHG density calculation for $Na_2CdGe_2S_6$.

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